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Post-print of a peer-reviewed article published by the Royal Society of Chemistry.
Published article available at: http://dx.doi.org/10.1039/C2JM33348A

Cite as:
Gromov, A., Gray, N., Szilagyi, P., & Campbell, E. (2012). Direct grafting of carbon nanotubes with ethylenediamine. *Journal of Materials Chemistry*, 22(39), 21242-21248.

Manuscript received: 24/05/2012; Accepted: 21/08/2012; Article published: 21/08/2012

Direct grafting of carbon nanotubes with ethylenediamine**

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[**]The authors thank the Engineering and Physical Sciences Research Council (EPSRC) for financial support (EP/I016686/1). EC acknowledges the WCU program of the MEST (R31-2008-000-10057-0). The help of Dr. Ronald Brown (School of Chemistry, University of Edinburgh, UK) with XPS analysis of the samples, Mrs. Sylvia Williamson (School of Chemistry, University of St.-Andrews, UK) with TGA analysis is gratefully acknowledged.

Supporting information:
[†]Electronic supplementary information (ESI) available: TEM image of MWCNTs used in this study; estimation of the carbon content in concentric MWCNT walls; SEM images of the EDA grafted MWCNT material; TEM images of pristine and EDA-functionalised carbon nanotubes; peak fit analysis of the XPS C1s area of pristine and EDA-functionalised carbon nanotubes; Raman spectra of pristine and EDA-grafted SWCNTs; Vis-NIR spectra of dispersions of pristine and EDA-grafted SWCNTs in DMF. See http://dx.doi.org/10.1039/C2JM33348A

Abstract

Singlewall and multiwall carbon nanotubes were covalently functionalised with ethylenediamine (EDA) in a simple one-pot process providing a good surface coverage. The successful grafting of EDA on carbon nanotubes (CNT) was shown by X-ray photoelectron spectroscopy (XPS), infra-red and Raman spectroscopy and thermogravimetric analysis (TGA). These functionalised CNT with terminal amino groups were shown to form composite polyamide materials with uniform CNT distribution in the polymer matrix.

Introduction

Introduction of functional groups onto the surface of carbon nanotubes (CNT) is essential for many existing and potential applications[1], such as improvement of CNT's solubility[2-5] in various solvents, reinforcement and thermal properties of polymers[6-19], sensing applications[20-28], bio-[29, 30] and medical applications[31, 32] etc.

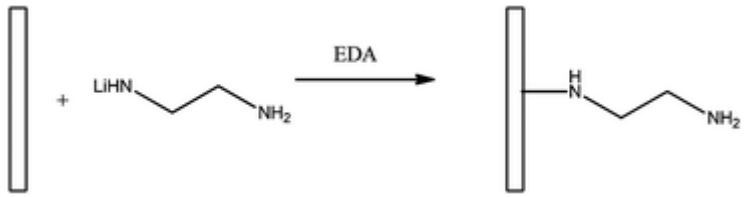
There is an increasing interest in the synthesis of CNT functionalised with substituents with multiple functional groups, e.g. ethylenediamine and other polyamines, because they may serve as useful precursors for further functionalisation. For example, CNT with terminal ethylenediamine moieties were successfully used for the production of metal nanoparticle based catalysts[33-38] and incorporated in epoxy-polymer matrices[39-42]. CNT modified with polyamines are promising materials for carbon dioxide capture[43-45].

The most common strategy for synthesis of multifunctional amino-derivatives consists of an oxidation step, leading to formation of carboxylic acid groups on the tube ends and defect sites, and the subsequent conversion of the acid groups to amides by using polyamines[13, 35, 37, 38, 46-53]. Alternative approaches include addition of amino- functionalities by substitution reactions with fluorinated carbon nanotubes[54-59], or sidewall CNT functionalisation with *in situ* generated diazonium derivatives of diamines[60-62].

There have also been a few publications concerning the direct covalent amino-functionalisation of CNT tips by exposure to vapours of amines[63, 64] at high temperatures and side-wall functionalisation of SWCNT using solutions of organic metal amides[65, 66] under mild conditions.

Lithium metal, with ethylenediamine as solvent, has been studied in the Benkeser hydrogenation[67, 68] and reductive alkylation/arylation[69] of CNT, however, no interaction of carbon nanotubes with ethylenediamine was considered and reported.

Here we report the simple one-pot grafting of both multiwall and singlewall CNT (MWCNT and SWCNT) with the 2-aminoethylamino substituent via direct interaction with ethylenediamine (EDA) or its mono lithium amide derivative (Li-EDA) as shown in scheme 1.



Scheme 1. Functionalisation of MWCNT with Li-EDA.

In comparison and addition to the lab-scale amination of SWCNT in the presence of primary amine and BuLi studied previously[65], our approach is more suitable for up-scaled production since it can be carried out at room or slightly elevated temperatures and, moreover, allows large volumes of highly flammable solvent such as THF or n-hexane to be avoided. In this paper we show the suitability of our method to SWCNT functionalisation, but focus mainly on finding the optimum conditions for the MWCNT covalent functionalisation, with moieties bearing multiple functional groups, which may be more interesting for materials applications.

Experimental

Materials. Elicarb MW high purity MWCNT powder and Elicarb SW high purity SWCNT were purchased from Thomas Swan &Co Ltd and were used in this study without further purification. According to manufacturer information (TEM†), MWCNT have a mean diameter of ca. 10 nm and consist of 5-8 walls. From these values we estimated that ca. 20% of carbon is present in the outer wall†.

Ethylenediamine (1,2-diaminoethane), anhydrous, laboratory grade reagent was purchased from Fisher Scientific. EDA was additionally shaken over calcium hydride and distilled over sodium metal prior to reaction.

Lithium metal, general purpose reagent, was purchased from Fisher Scientific. Li was washed in hexane from mineral oil prior to reaction.

Terephtaloyl chloride (TPC, 97%), diethylenetriamine (DETA, 98%) and polyvinyl alcohol (PVA, 88% hydrolyzed, MW 88000 Da) were purchased from Arcos Organics and used without additional purification.

MWCNT grafting with EDA. 60 ml of dry EDA (0.9 mol) was placed into a nitrogen-purged heat-dried reaction flask. 50 mg of Li (7.2 mmol) were added in small portions at room temperature. Dissolution of Li was fast and accompanied by formation of a blue solution (solvated electron). The temperature of the reaction mixture at this point was slightly increased (< 40 ^{o}C) until the blue colour of the solution disappeared, indicating the formation of Li-EDA. 50 mg of MWCNT (4.2 mmol C) powder was added quickly to the Li-

EDA solution in EDA under strong stirring (1200 rpm) at room temperature; the resultant suspension was stirred at room temperature overnight, and then heated for 4 - 5 h (see table 1 for details). The reaction mixture was quenched by bubbling air for 2 h, the excess of Li-EDA was then decomposed by adding 15 ml of methanol and 50 ml of water at 15 ^{o}C. The MWCNT material was isolated by filtration (PTFE membrane 0.2 μm), washed with water 3x50 ml, methanol, and dried in a vacuum desiccator for 48 h. Samples were stored in dry nitrogen atmosphere.

Table 1. XPS data of pristine MWCNT and MWCNT functionalised with EDA or Li-EDA at different temperatures.

Reagent	-	-	-	EDA		Li-EDA/EDA			
Reaction conditions	Pristine MWCNT	Pristine MWCNT, washed in NMP	Purified MWCNT	20 ^{o}C	70 ^{o}C	20 ^{o}C	40 ^{o}C	55 ^{o}C *	70 ^{o}C
XPS data (at. %)	C 99.52 O 0.48	C 98.69 N 0.15 O 1.15	C 97.55 O 2.45	C98.59 N 0.3 O 1.11	C95.11 N 1.42 O 3.47	C 95.46 N 1.72 O 2.82	C 94.54 N 3.21 O 2.26	C 82.77 N 2.68 O14.55	C 96.26 N 2.24 O 1.5

* - this sample was stored in air; it is assumed that most of the oxygen in the sample originates from CO_2 captured with basic amino groups; the corrected composition of CO_2-free material corresponds to C 94.75 at%, N 3.33 at% and O – 1.93 at%. All other samples were stored under dry nitrogen.

Reaction of Li-EDA with SWCNT (13 mg of SWCNT, 21 mg of Li in 60 ml EDA) was carried out at 55 ^{o}C for 10h in dry nitrogen atmosphere; all other details were similar to the procedure shown above.

Purification of MWCNT. MWCNTs were treated in 'piranha' solution (conc. H_2SO_4 and 30% H_2O_2, 4:1 v/v) at 40-45°C for 5 hrs. MWCNTs were isolated by vacuum filtration through 0.2 μm PTFE membrane, washed in turn with water, 3% NaOH, water, 5% HCl, water and methanol. The 'piranha'-treated MWCNT material was then annealed at 350°C for 3.5 hrs in an argon atmosphere.

Formation of CNT-polyamide microspheres. 0.7 mg of EDA grafted MWCNT (est. 0.0007 mmol of terminal NH_2 groups) were added to the solution of ~50 mg TPC (0.246 mmol) in 10 ml of toluene and the mixture was sonicated for 10 min. at 0^{o}C. 3ml of aqueous solution containing 650 μl of DETA (6 mmol) and 3 mg of PVA was added dropwise to the above prepared CNT dispersion in toluene under stirring (1100rpm). The mixture was stirred for 3 min. and then was left additionally without stirring for 20 min. Microcapsules were collected on filter paper.

A comparison of the interaction of EDA grafted MWCNT (further denoted as CNT-EDA) and pristine MWCNT with TCP and formation of CNT/polyamide composites from both nanotube materials was carried out. 2.2 mg of CNT-EDA (est. 0.0025 mmol NH_2 groups) were added to a solution of ~70 mg (0.35 mmol)

TPC in 40 ml dichloromethane (DMC); the mixture was sonicated for 10 min at 0^{o}C and then stirred for 1 h at r.t. CNT material after this treatment was collected by filtration on a PTFE membrane, then re-dispersed under sonication in a methanol/water mixture (3:1) for 15 min., filtered again, washed with DMF and methanol and dried in vacuum. The similar procedure was used for pristine MWCNT (3.3 mg of MWNT and 66.5 mg of TPC (0.32 mmol) in 40 ml DCM).

CNT/polyamide composites were prepared by adding 650 μl (6 mmol) of DETA in 1 ml H_2O to the CNT-TPC dispersion (prepared as described above from 0.8 – 1.2 mg of either pristine MWCNT or CNT-EDA and ~50 mg of TPC) in 10 ml toluene under moderate stirring for 30 min. The obtained polyamide flakes were collected on filter paper and dried in air as a thick layer.

Analysis. XPS spectra were taken using a VG Sigma Probe instrument with a monochromated Al K alpha Source. C1s peak fit analysis of carbon nanotube species was performed using Renishaw Wire2 software.

FT-IR spectra were measured on a Smiths IlluminateIR microscope equipped with Smiths Detection ARO objective (x10); the IR spot size was 100μm; the samples for IR measurements were prepared by drop casting thick dispersions of carbon nanotube materials in DMF on IR-reflective low-E glass slides. CNT IR spectral features have low intensity (on the level of 0.01 absorption units) and for all spectra a baseline subtraction procedure was used. The assignment of IR spectra was performed using IR and Raman charts.[70]

Raman spectra were measured using a Renishaw inVia Raman microscope. The dry CNT samples, prepared by drop-casting on polished silicon wafers, were measured in a backscattering configuration. For D/G ratio estimation, an excitation wavelength of 785 nm was used. The peak area ratio D/G was the average of 3-4 spectra taken at different spots on each sample. Analysis of spectra was performed with the use of Renishaw Wire2 software. Raman spectra of CNT/polyamide composites and microcapsules were taken using an excitation wavelength of 514 nm.

Thermogravimetric analysis (Netzsch STA 449C) was carried out under an oxidising atmosphere (in air) with a flow rate of 30 sccm.

SEM images of microcapsules were taken on a Philips XL30CP instrument equipped with a tungsten filament as electron beam source; the samples were gold coated prior to SEM imaging.

Results and discussion

The interaction of MWCNT with the mono-lithium derivative of ethylenediamine (Li-EDA) in dry EDA solvent was investigated under different conditions (at 20/40/55/70 ^{o}C). XPS analysis of MWCNT after treatment with Li-EDA showed an increased nitrogen content (1.7 - >3 at %) with respect to pristine MWCNT. To ensure that this is not the result of EDA physisorption to MWCNT, the reaction similarly was

carried out also in dry EDA in the absence of Li at temperatures of 20°C and 70°C. In this case nitrogen content was 0.3 at% for the sample treated with EDA at 20 °C and >1.4 at % for the MWCNT treated with EDA at 70 °C. Additionally, the sample of pristine MWCNT was treated (bath sonication 0.5 h) with nitrogen containing solvent N-methyl-2-pyrrolidone (NMP).

The interaction of Li-EDA with MWCNT appeared to be very sensitive to moisture. When the reaction was performed in wet EDA (no blue solution observed during the dissolution step of Li in EDA, MWCNT treatment in EDA/Li-EDA/LiOH at 40°C) the nitrogen content in the product was much smaller (0.74 at%) compared to the process carried out in dry EDA.

XPS data are summarised in table 1.

The detailed analysis of of C1s peak components (in the range of 284 - 291 eV)† clearly exhibited the significant increase of the peak around 285.7 eV in Li-EDA treated MWCNTs relatively to pristine MWCNT and material treated with EDA in the absence of Li at 20°C, which are looking very similar.

From XPS data it can be concluded that the increase of nitrogen content originates from the covalent functionalisation of the MWCNT outer shell with EDA and is not due to physisorption of solvent, the limit of which was, probably, observed in the MWCNT sample treated with EDA at 20°C.

IR spectroscopy also provides strong evidence for the introduction of EDA moieties onto MWCNT walls. The IR spectra of EDA-functionalised species, showing increased nitrogen content, clearly exhibit new bands in the region 1500 – 1650 cm^{-1} (not visible in the IR spectra from pristine MWCNT) which can be attributed to N-H deformation vibrations, and the bands in the regions 3100 - 3270 cm^{-1} and 2910 -2970 cm^{-1}, which can be attributed N-H and C-H stretching respectively (fig.1).

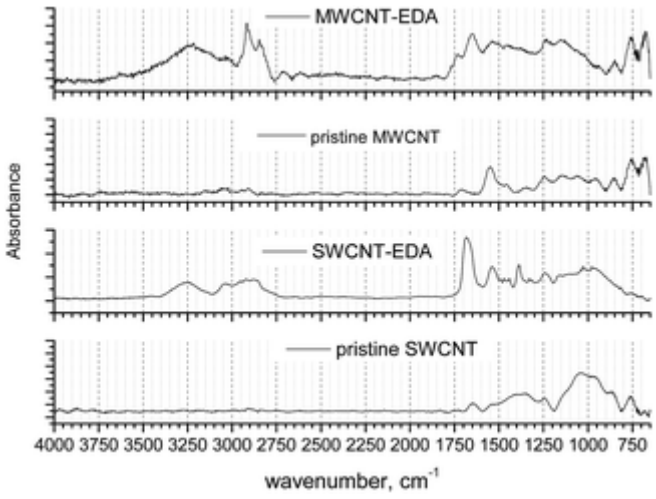


Figure 1. FTIR spectra of (from bottom to top) pristine SWCNT, the product of the reaction between SWCNT, pristine MWCNT and the product of the reaction between MWCNT with Li-EDA (40°C).

The spectrum of EDA-functionalised MWCNT exhibits features that are similar to those of pristine EDA[71] and are in good agreement with literature data concerning MWCNT functionalised with amines[64].

For Raman analysis, the MWCNT sample was sonicated (0.5 h in ultrasonic bath) in nitrogen containing solvent N-methyl-2-pyrrolidone (NMP), then isolated by centrifugation and washed from NMP with methanol. It could be expected that sidewall functionalisation would result in an increase of the Raman D-to-G peak ratio in the material due to the creation of new defects in the hexagonal carbon lattice[72]. However, there are known examples in literature, showing that in the case of MWCNT, covalent[73, 74] or even non-covalent[74] (e.g. dispersion in solvent) functionalisation at CNT defect sites may decrease the D-to-G ratio, perhaps, due to some purification effect resulting in removal of non-MWCNT carbon content. Indeed, the non-destructive treatment of pristine MWCNT with NMP, or EDA in the absence of Li at 20°C (which didn't result in grafting as shown by XPS), or purification of MWCNT by concecutive oxidation/annealing procedure led to significant decrase D-to-G peak ratio in the material. Thus, although in all our functionalised samples, the peak area D-to-G ratio was smaller than in the pristine MWCNT, if to make a comparison with the purified MWCNT or material first sonicated in NMP, there is a clear trend of increasing D/G with an increase of the nitrogen content in the sample. The correlation between the D/G ratio and the content of atomic nitrogen in the sample is shown in fig.2.

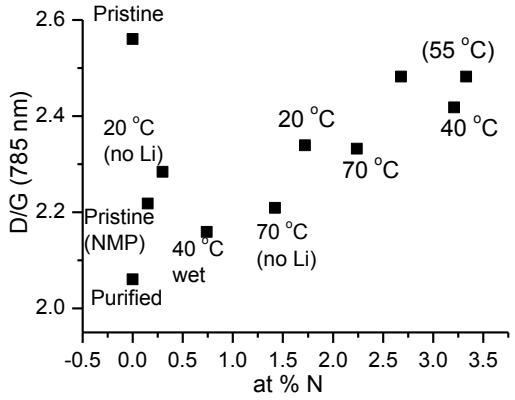


Figure 2. D/G (peak area ratio) in MWCNT's as a function of nitrogen content in the sample.

The MWCNT used in this study have 5-8 carbon shells and diameters of approximately 10 nm, resulting in approximately 20% of the available carbon being present in the outer shell.† Thus, in the samples with >2% N, the functionalisation degree should be ca. one -$NHCH_2CH_2NH_2$ group per 12-20 C atoms of the outer shell (5-8% of surface coverage).

In the samples with low nitrogen content (<1.5% -interaction with EDA, no Li, 70 °C) the functionalisation

degree (≤ 3% surface coverage) is comparable with the reported density of defects for CVD grown MWCNT.[75-77] Thus, it is possible to conclude that for the reaction of MWCNT with EDA in the absence of Li at elevated temperatures, functionalisation affects only MWCNT defect sites, while interaction with Li-EDA results in genuine sidewall functionalisation (i.e. creation of new "defects" in terms of Raman activity of D-phonon).

TGA was carried out in air for the MWCNT samples treated with Li-EDA/EDA at 40 and 70°C (fig.3a). For both samples, the first small weight loss step (~5-7 % of mass) started at ≥250°C and complete burning of the carbon nanotube body occurred at 530 – 560 °C. For pristine MWCNT the first weight loss was observed above 400 °C and complete burning occurred around 600 °C, which is 50-70°C higher than for the functionalised material. This supports the above conclusion concerning the formation of additional defects on the walls of MWCNT with high (>2 %) content of nitrogen.

SWCNT under treatment with Li-EDA in EDA solvent also get functionalised , similar to MWCNT. XPS analysis of the isolated SWCNT product showed C 89.5%, N 4.49% and O 6.01%, that is consistent with addition of one -$NHCH_2CH_2NH_2$ group per ~35 carbon atoms of the hexagonal lattice. The IR spectrum of the functionalised SWCNT (fig.1) shows new bands in the regions 1470 – 1650 cm^{-1} (N-H bending vibrations), 3270 cm^{-1} (N-H stretching) and 2910 -2970 cm^{-1} (C-H stretching), compared to pristine SWCNT. Raman spectra of functionalised SWCNT† show an increase of the D/G ratio with respect to pristine SWCNT (0.27 vs 0.23 respectively). TGA of functionalised and pristine SWCNT (fig. 3b) demonstrated a very different behaviour: in functionalised SWCNT a weight loss of ca. 3% happened in the temperature range 100-350 °C and complete nanotube burning proceeded slowly between 490 and 700 °C. In contrast, pristine SWCNT exhibit a small weight increase (~7%) up to the temperature 390 °C due to chemisorption of oxygen[78], and the fast burning happened between 535 and 640 °C.

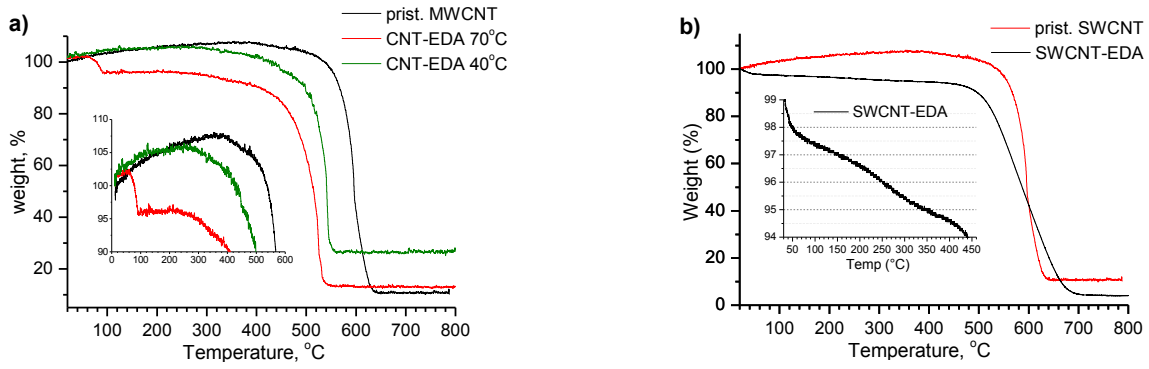


Figure 3. a) TGA profiles of pristine (black) MWCNT and material treated with Li-EDA at 40°C (green) and 70°C (red); b) TGA profiles of pristine (red) SWCNT and material treated with Li-EDA (black). The insets show an expanded y-scale to more clearly demonstrate the early stages of weight-loss. TGA was carried out in air.

Additionally, according to Vis-NIR absorption spectra, EDA grafted SWCNT show higher solubility in DMF than pristine SWNT material.†

In the presence of terminal amino groups on the surface of EDA grafted MWCNT one could expect better CNT dispersibility in a polymer matrix[6, 79, 80], especially in the case of *in situ* polycondensation of derivatives of polycarboxylic acids with polyamines due to direct chemical integration. Therefore, we compared the behaviour of EDA grafted MWCNT and pristine MWCNT for their ability to form homogeneous polyamide composites.

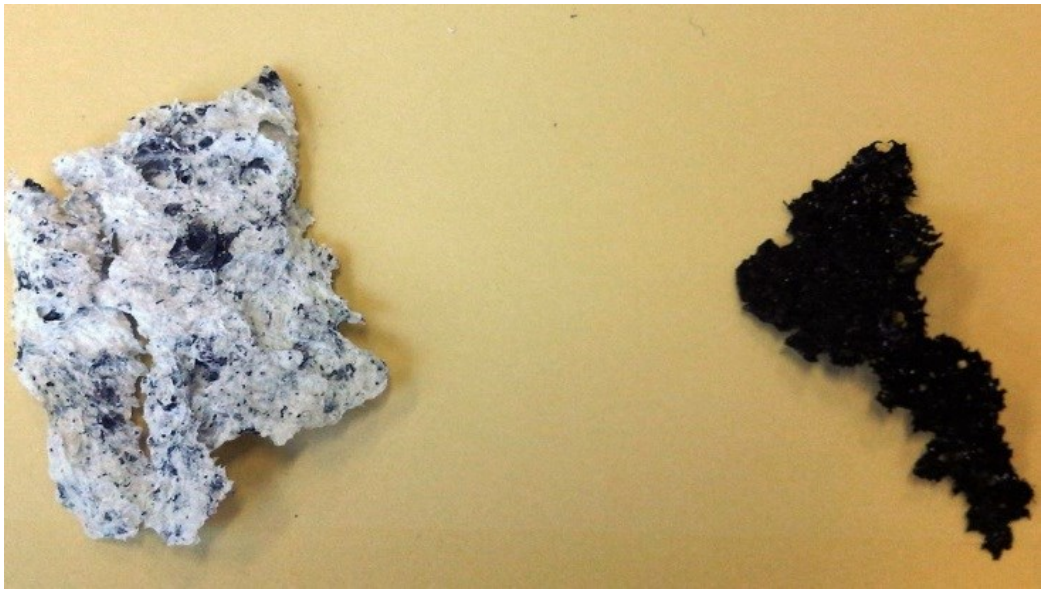


Figure 4. Photograph of samples of polyamide prepared by *in situ* polycondensation of terephtaloyl chloride (TPC) and diethylenetriamine (DETA) in toluene/H_2O in the presence of pristine MWCNT (left) and EDA grafted MWCNT (right) (for details see text).

Fig. 4 shows polyamide films prepared in the presence of pristine MWCNT and EDA grafted MWCNT. The polyamide material prepared with EDA functionalised MWCNT after collection on filter paper and drying looked homogeneously black, while the one obtained in the presence of pristine MWCNT clearly exhibited black CNT 'islands' incorporated within the polymer matrix.

The different behaviour follows from intermediate fuctionalisation of MWCNT-EDA with terephtaloyl chloride (TPC) which doesn't happen in the case of pristine MWCNT. Fig. 5 shows FTIR spectra of pristine MWCNT and MWCNT-EDA before and after treatment with excess of TPC.

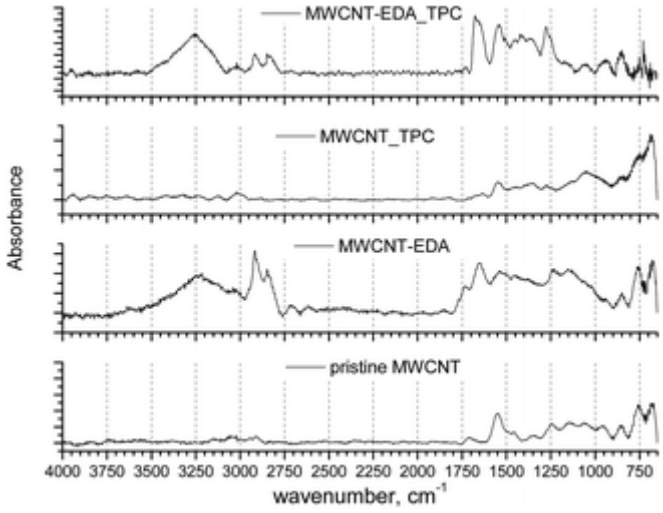


Figure 5. FTIR spectra of (from bottom to top): pristine MWCNT, EDA grafted MWCNT (MWCNT-EDA), pristine MWCNT treated with terephtaloyl chloride (TPC) and MWCNT-EDA treated with TPC (for details see text).

From the FTIR spectra it is clear that pristine MWCNT and TPC treated MWCNT after carefully washing out the excess of TPC are practically identical. In comparison to untreated MWCNT-EDA material, the material treated with TPC shows the appearance of a new strong band around 1680 cm^{-1}, which can be attributed to C=O vibrations of both aromatic amide and carboxylic acid groups, a band around 1280 cm^{-1}, due to C-O stretching in a carboxyl group and several bands in the region 1400-1500 cm^{-1} arising from vibrations of an aromatic ring.

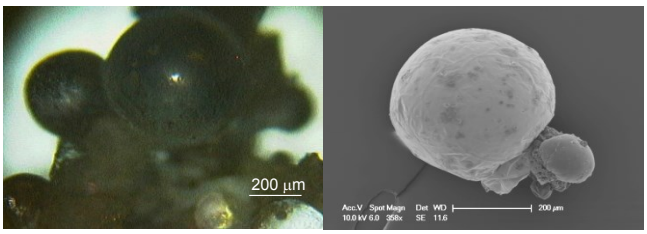


Figure 6. Optical microscope image (left) and SEM image (right) of polyamide-CNT microcapsules, with CNT content in the shell 1.2-1.4%.

The reaction of TPC treated MWCNT-EDA with DETA in the presence of an emulsifying agent (PVA) led to the formation of microcapsules with diameters in the range of ~0.2 -0.5 mm with the shells built from CNT-polyamide composite.

Raman spectra of microcapsule shells (fig.7) show features characteristic to both EDA functionalised MWCNT, i.e. D, G and G' peaks at 1350, 1585 and around 2700 cm^{-1} respectively, and polyamide material with peaks around 1300 cm^{-1} (amide III band, 1440 cm^{-1} (C-H bending), 1613 cm^{-1} (1,4-disubsituted aromatic ring vibrations), 1650 cm^{-1} (amide I band), 2960 and 3775 cm^{-1} (C-H stretching from aliphatic and aromatic moieties).

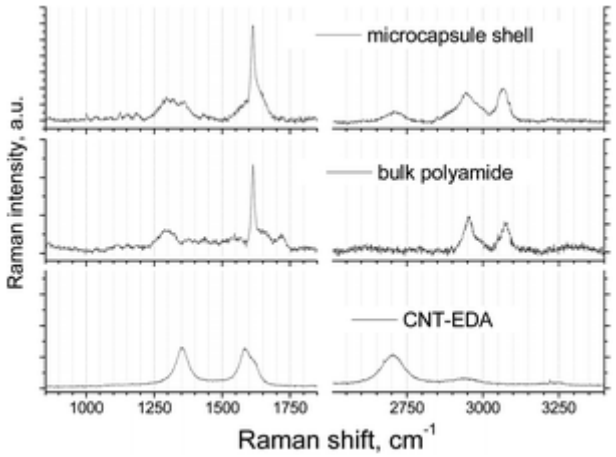


Figure 7. Raman spectra (from bottom to top) of MWCNT grafted with EDA at 55°C, product of condensation of terephtaloyl chloride(TPC) with diethylenetriamine (DETA), and the surface of microcapsule shell built of CNT-polyamide composite. The spectra were taken with an excitation wavelength of 514 nm.

The measurements of Raman spectra from the microcapsule shells required the use of microscope objectives with narrow depth of field (i.e. with high magnification and large numerical aperture); otherwise, in most cases, only the spectrum of toluene, filling the microcapsules[81] was recorded.

It was reported[81] that a similar method of microcapsule preparation in the presence of pristine MWCNTs resulted in encapsulation of CNT material inside microcapsules. In such systems a cargo-release mechanism was based on increased pressure inside the microcapsule causing the shell to burst open, triggered by the heating of pristine MWCNTs due to laser irradiation[81]. Contrary to that, the use of MWCNT-EDA material yielded microcapsules with the shell built of MWCNT-polyamide composite with MWCNT content of 1.2 – 1.4% (according to the load of reagents and process stoichiometry). We anticipate that the functionalised MWCNTs covalently bound in the microcapsule shells may enable its opening independently of the medium inside the microcapsule and, thus, avoiding significant heating of the microcapsule cargo.

Conclusions

In conclusion, we have shown the possibility of a simple one-pot sidewall functionalisation of MWCNT and SWCNT with Li-EDA in EDA solvent under moderate heating. In contrast, Li-EDA in EDA solvent at room temperature as well as pristine EDA (without Li) at elevated temperatures affects only existing defect sites on MWCNT walls. The direct one-pot MWCNT reaction with EDA moieties provides good surface coverage and may be used as a simple alternative to existing methods for attaching multifunctional groups onto carbon nanotubes. The presence of terminal amino groups in CNT-EDA was utilized in the formation of CNT-polyamide composite materials with uniform CNT distribution in the polymer matrix and preparation of microcapsules with CNT-polyamide composite shells.

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